Center for Hydrogen Storage Research at Delaware State University

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Project ID #
STP_43_Goudy

Overview

Timeline

- Start – June 1, 2006
- Finish – May 30, 2010
- 75% complete

Budget

- Total project funding
  - DOE $990 K
  - DSU $247.5 K
- Funding received as of FY 08
  - $757 K
- Funding for FY09
  - $ 233 K

Barriers

- Barriers addressed
  - Weight and Volume
  - Durability
  - Refueling Time
  - Hydrogen Capacity and Reversibility

Partners

- Interactions/ collaborations
  - Georgia Tech
  - University of Pittsburgh
  - University of Delaware
  - Air Liquide

Relevance

- The objectives of this project are to:
- Identify complex hydrides that have the potential to meet DOE's goals for storage and demonstrate the optimum temperature and pressure ranges under a variety of conditions.
- Improve the sorption properties of systems that have been identified as good prospects for hydrogen storage.
- Determine the cyclic stability of new materials and develop strategies for improving reversibility.
- Perform kinetic modeling studies and develop methods for improving kinetics and lowering reaction temperatures, thereby reducing refueling time.
- Extend the studies to include other complex hydrides, that have greater hydrogen storage potential.

Approach

- Task 1 – Design suitable methods using $LiBH_4/MgH_4$ as a model system
  - Synthesis of new materials by mechanical alloying using ball milling
  - Determine thermal stability using TGA or TPD.
  - Use XRD to determine phase purity and crystal structure
  - Use PCI analyses to determine thermodynamic stability

- Task 2 – Find catalysts for making the hydriding faster and reversible

- Task 3 - Kinetic modeling study
  - Determine kinetic rate curves using constant pressure driving forces
  - Perform modeling to gain understanding of the mechanism

- Task 4 – Study other classes of promising hydrogen storage materials
  - Focus on destabilized hydride materials such as systems of general composition $MM'_{m-n}(BH_4)_m$ (M= Cu, Mn and Zr, M'= Li or Na) and others with reaction enthalpies less than 50 kJ/mol H_2.

Approach/Milestones

Year	Milestone or Go/No-Go Decision
2006	Milestone: The methods and procedures to be used for testing and characterizing complex hydrides using $NaAlH_4$ as a model system were completed.
2007	Go/No-Go decision: It was decided that most of the effort should be expended on studying the borohydride systems for hydrogen storage instead of the alanates.
2008	Milestone: It was discovered that the $CaH_2/LiBH_4$ system could reversibly absorb and release approximately 9 weight percent hydrogen, with a desorption enthalpy of 63 kJ/mol H_2. It was also found that certain ternary mixtures could release hydrogen at significantly lower temperatures but they were not reversible.
2009	Go/No-Go Decision: We decided not to continue studies on ternary borohydride systems that contain amides. We will continue to focus on other borohydride systems with reaction enthalpies predicted to be less than 50 kJ/mol H_2.

Technical Accomplishments/ Progress/Results

- Cycling studies done on the $LiBH_4/CaH_2$ system at 450^oC indicate that the absorption capacity decreases from 9 weight percent hydrogen to less than 3 percent after 25 cycles
- The hydrogen sorption characteristics of systems of general composition $MM'_{m-n}(BH_4)_m$ (M= Cu, Mn and Zr, M'= Li or Na) have been studied. The Mn-containing material was found to release hydrogen at about 130^oC but there was also some evidence of diborane release as well. These materials were stable solids under the conditions used.
- Kinetics studies were done on the $MgH_2/LiBH_4$ system, with varying amounts of $LiBH_4$, to determine desorption rates using constant pressure driving forces. The rates were found to decrease with increasing amounts of $LiBH_4$ in the system.

Accomplishments

Preparation and Characterization of Double Cation Borohydride Materials

Techniques Used

- **IR**
- **TGA**
- **TPD**

Systems Studied

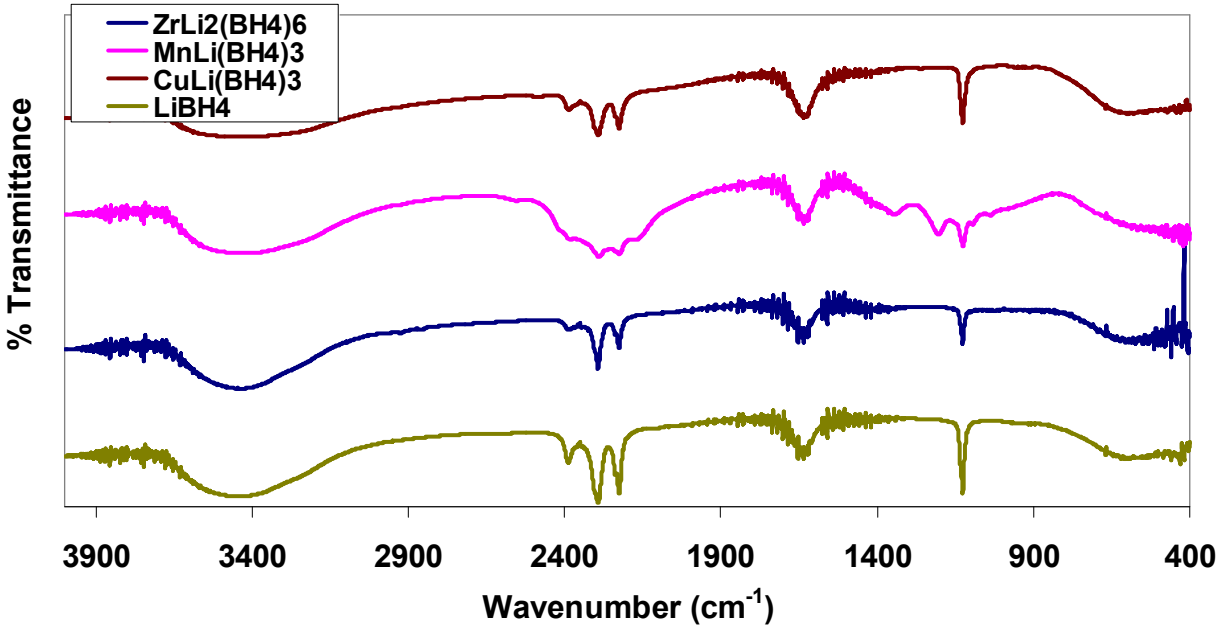
- **$MLi_{m-n}(BH_4)_m$**
- **$MNa_{m-n}(BH_4)_m$**
- **(M=Cu, Mn and Zr)**

- **$Mn(BH_4)_2$**
- **$MnLi(BH_4)_3$**
- **$MnNa(BH_4)_3$**

- All samples were prepared by ball milling $LiBH_4$ or $NaBH_4$ with $MnCl_2$. XRD and FTIR were used to characterize the final product mixtures. The product mixtures were all stable solids.
- Goal: To compare the desorption characteristics and correlate them with possible differences in bonding characteristics

Accomplishments

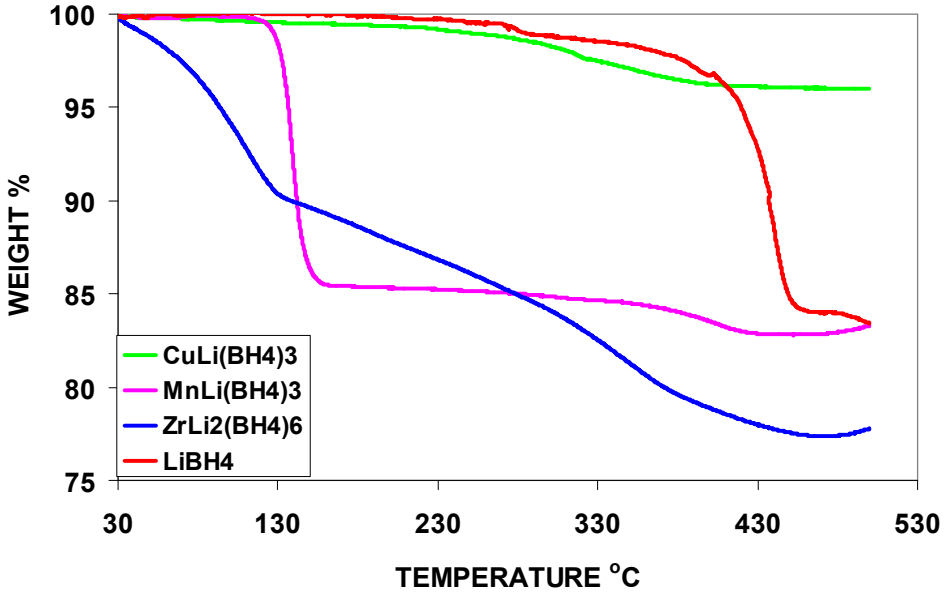
IR spectra of $LiBH_4$, $CuLi(BH_4)_3$, $MnLi(BH_4)_3$ and $ZrLi_2(BH_4)_6$



- The spectra are all similar but the Mn-containing complex displays two peaks in the 1200 – 1400 cm^{-1} region that are absent in the others. This indicated that the bonding is similar in each complex but the Mn-complex may have some unique characteristics.

Accomplishments

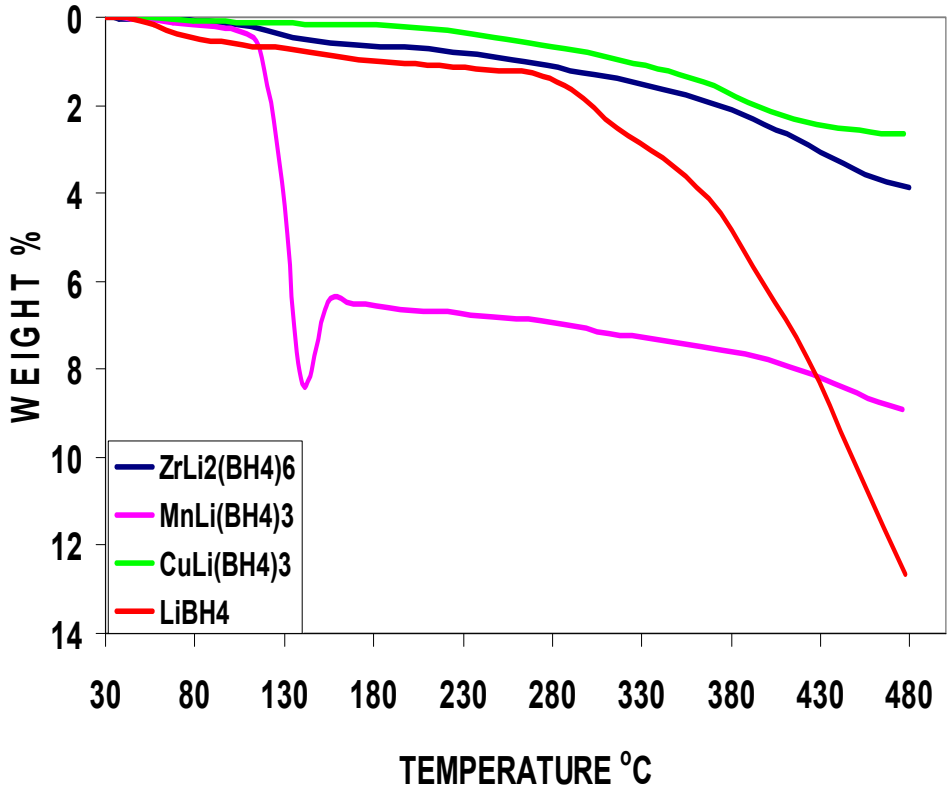
Composite TGA Plot of MLiBorohydrides,(M= Cu, Mn & Zr)



- TGA analysis shows that the Mn-containing borohydride begins to release hydrogen at about 130 C but the unusually large weight loss indicates that some diborane may be released as well. The Zr-containing compound begins to lose mass near room temperature but this is likely caused by vaporization of the sample. The Cu-containing sample releases hydrogen at elevated temperature.

Accomplishments

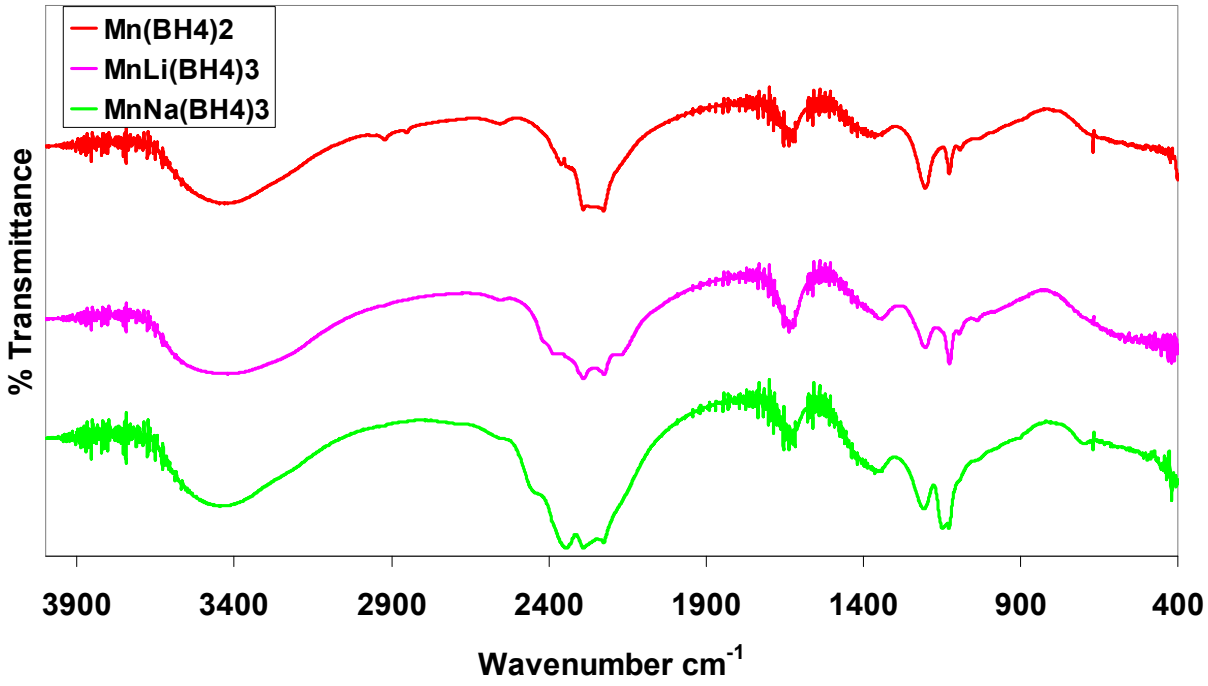
TPD curves for $CuLi(BH_4)_3$, $MnLi(BH_4)_3$, $ZrLi_2(BH_4)_6$, and $LiBH_4$



- The desorption temperatures for the TPD curves are in general agreement with those in the TGAs. However, the decrease in weight % is less, possibly due to a higher hydrogen back pressure in the PCI apparatus. The curve for $MnLi(BH_4)_3$ displays an unexplained weight gain at one point.

Accomplishments

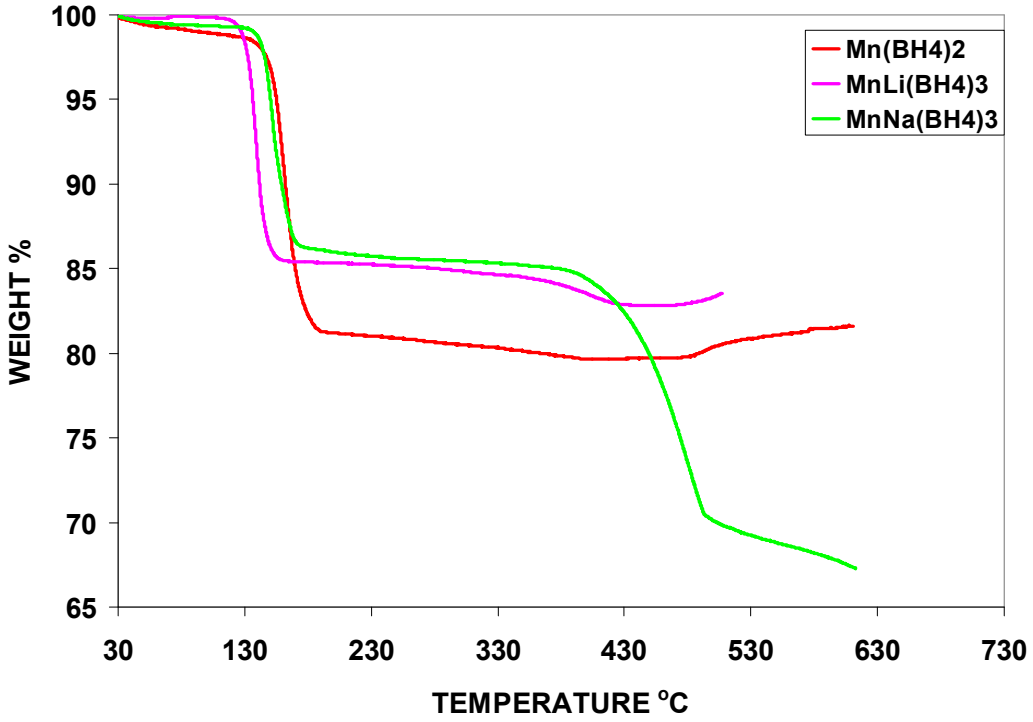
IR spectra of $Mn(BH_4)_2$, $MnLi(BH_4)_3$ & $MnNa(BH_4)_3$



- A comparison shows no significant differences in these spectra. This indicates that the Li or Na substituent has little effect on the bonding

Accomplishments

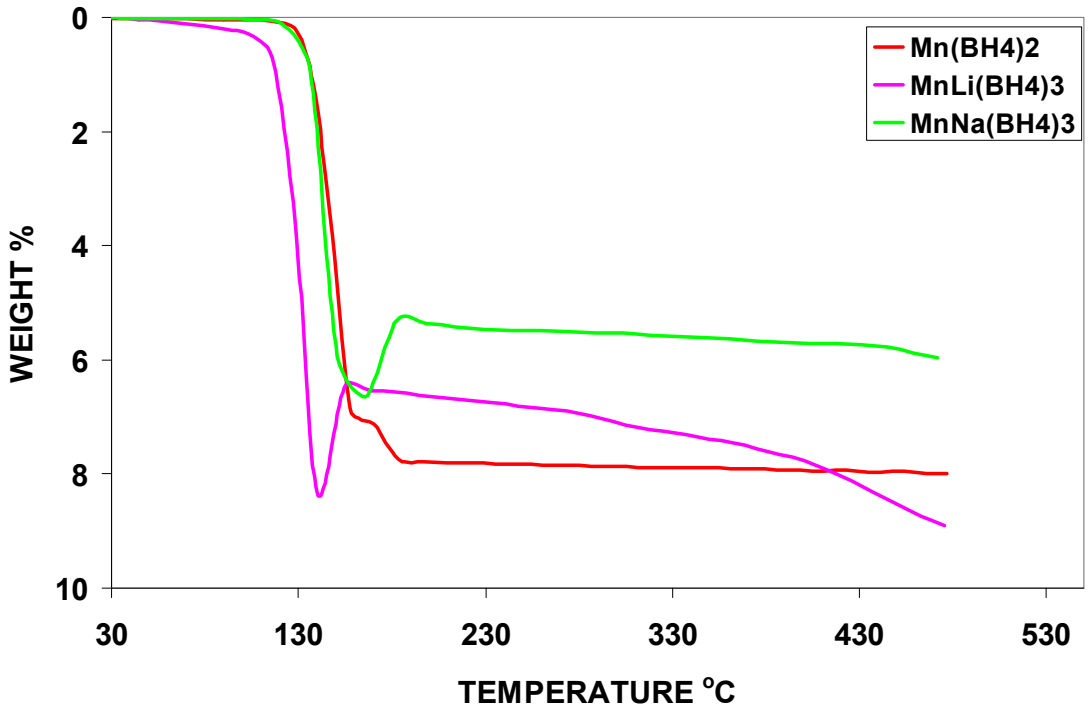
TGA Curves of $Mn(BH_4)_2$, $MnLi(BH_4)_3$ & $MnNa(BH_4)_3$



- The graphs show that there are no significant differences in the desorption temperatures of the complexes. The larger than expected decrease in the weight % of these samples, especially $MnNa(BH_4)_3$ above 400 C, may be caused by diborane release.

Accomplishments

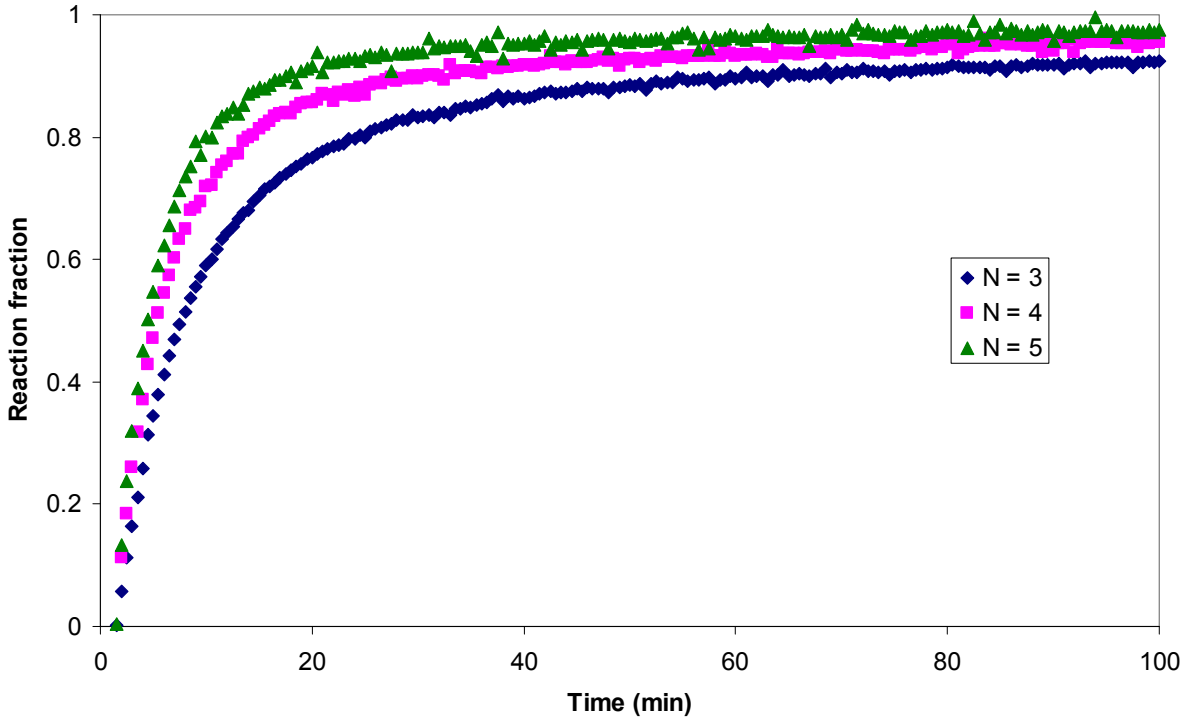
TPD Plot of $Mn(BH_4)_2$, $MnLi(BH_4)_3$ & $MnNa(BH_4)_3$



- The desorption temperatures of the complexes are in general agreement with those seen in TGA and the decreases in weight % are more in line with the expected amounts. Diborane release may less of a factor at the higher back pressures in the PCI apparatus.

Accomplishments

Desorption Kinetics of the $MgH_2/LiBH_4$ System



- Lower plateau reaction at 450 C and N = 3, 4, and 5. The N-value is defined at the ratio of the dissociation plateau pressure to the applied hydrogen pressure

Collaborations

- Collaborators
  - The University of Pittsburgh and Georgia Tech: Theoretical calculations done by Karl Johnson and David Scholl, as well as many discussions with them, have been very useful in helping us choose what systems to focus on.
  - The University of Delaware and Air Liquide: Suresh Advani's group is working with us in an effort to determine the feasibility of testing some hydrogen storage materials in an actual hydrogen powered vehicle.

Future Work

- In the FY 09-10, the following are planned
  - Prepare and do thermal analysis on borohydride systems with reaction enthalpies less than 50 kJ/mol H_2
  - Improve reaction kinetics and reversibility of sample systems with general composition $MM'_{m-n}(BH_4)_m$ by using nanotechnology.
  - Determine the cyclic stability of complex hydrides to determine end-use suitability. Techniques such as TPD and RGA will be used extensively in these efforts.
  - Perform reaction kinetics and modeling studies on systems that have the desired properties for hydrogen storage.
  - Perform thermodynamic measurements, such as PCI analyses, on samples found to be reversible.

Project Summary

Relevance:	The materials under consideration in this study have the potential to meet the on board hydrogen storage goals established by the DOE. Issues such as reaction temperatures, reaction rates and reversibility are being addressed since they are important in practical uses.
Approach:	Borohydrides containing Li and Cu, Zr or Mn were prepared and characterized by TGA, TPD and IR to compare their hydrogen sorption characteristics and determine their suitability for hydrogen storage.
Technical Accomplishments:	Have demonstrated that LiMnBorohydrides may be suitable for hydrogen storage. Will develop a method to eliminate the diborane gas that is produced and thereby achieve greater reversibiltiy. Kinetic studies have been initiated on the $MgH_2/LiBH_4$ system.
Proposed Future Research:	Studies will focus on several destabilized hydride systems that are predicted to absorb greater than 6 weight percent H_2 and have reaction enthalpies less than 50 kJ/mol H_2. Nanotechnology will be used to reduce diborane release.